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by

J. H. Gibson
Natural Resource Ecology Laboratory
Colorado State University
Fort Collins, CO 80523

R. A. Linthurst
Department of Botany
North Carolina State University
Raleigh, NC 27650

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R. W. Wilhour

Environmental Research Laboratory
Officer of Research and Development
U.S. Environmental Protection Agency
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16. ABSTRACT Since the mid 70's there has been a growing concern in the U.S. and Canada about the widespread deposition of acidic materials from the atmosphere. Acid rain is now found over most or all of the northeastern U.S. and southeastern Canada. As we rely more heavily on coal as our major energy source, it is likely that this problem will become more widespread. A major response in both Canada and the U.S. has been the organization of nationwide monitoring programs to assess the geographic and temporal trends in chemical deposition and the initiation of surveys and research efforts to determine current and future impacts on aquatic and terrestrial systems.

Both U.S. & Canada monitoring studies show the presence of acid rain in western areas, but at levels several times less acidic than in the east. Surveys based on geological materials and soil types indicate sensitive areas in both countries. Gradual acidification of lakes and streams has seriously affected fish populations in some areas. Leaching of aluminum, heavy metals & plant nutrients from soils affect water quality & may have implications with respect to reduced forest productivity. Extensive programs are underway to determine the extent of potential damage to crops and economic losses. Many other research efforts are underway in both countries to assess both beneficial and detrimental impacts of chemical deposition.

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EFFECTS OF ACIDIC PRECIPITATION ON THE NORTH AMERICAN CONTINENT

J. H. GIBSON[1] and R. A. LINTHURST[2]

[1]Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado 80523

[2]Department of Botany, North Carolina State University, Raleigh, North Carolina 27650

ABSTRACT

Since the mid 70's there has been a growing concern in the U.S. and Canada about the widespread deposition of acidic materials from the atmosphere. Acid rain is now found over most or all of the northeastern U.S. and southeastern Canada. As we rely more heavily on coal as our major energy source, it is likely that this problem will become more widespread. A major response in both Canada and the U.S. has been the organization of nationwide monitoring programs to assess the geographic and temporal trends in chemical deposition and the initiation of surveys and research efforts to determine current and future impacts on aquatic and terrestrial systems.

Both U.S. and Canadian monitoring studies show the presence of acid rain in the western states and provinces, in addition to the east, but at levels several times less acidic than the eastern areas. Surveys based on geological materials and soil types indicate the existence of sensitive areas in the northeastern U.S. and Canada and western regions of both countries. In these sensitive areas in the east which are receiving the highest levels of acid deposition there appear to be a significant number of lakes and streams undergoing gradual acidification. In some areas this has seriously affected fish populations. Other studies are concerned with the leaching of aluminum, heavy metals and plant nutrients from soils which affect water quality and may have implications with respect to reduced forest productivity. Extensive programs are underway to determine the extent of potential damage to agricultural crops and subsequent economic losses. Many other research efforts are underway in the U.S. and Canada to assess both the beneficial and detrimental impacts of chemical deposition.

INTRODUCTION

In 1976, Likens (ref.1) published pH isopleth maps for the eastern United States showing extensive areas receiving rainfall with pH levels below 5.6. In areas of the northeastern U.S. and southern Ontario the mean annual pH of rainfall was as low as 4.2. This data covered the period 1972 to 1973 and was obtained from a variety of independent monitoring studies. Likens showed that, when compared to similar data obtained by Junge during the period 1955 to 1956, the acidity of precipitation had increased in eastern U.S. and that regions of the U.S. receiving rainfall of pH of less than 5.6 now extended into the southeast and a portion of the midwest. This information along with

results of studies on the decline of fish populations in lakes of the northeastern U.S. and southeastern Canada has led to major national concerns in both countries over the effect of acidic precipitation. It has now been well documented in North America, as in Europe and Scandinavia, that the increase in acidity is a result of increased atmospheric loading of sulfate and nitrate compounds resulting from the combustion of fossil fuels. In this discussion we will attempt to describe the development of efforts to determine the extent of atmospheric deposition both spatially and temporally in both U.S. and Canada and to identify major effects and/or research topics now being investigated related to aquatic and terrestrial ecosystems.

Spatial and Temporal Trends in Atmospheric Deposition

In both the United States and Canada, major national monitoring networks have been organized to assess spatial and temporal trends in atmospheric deposition. The CANSAP network (Canadian Network for Sampling Precipitation) organized in 1977 and the NADP network (National Atmospheric Deposition Program) organized in 1978 have established 50 and 100 stations, respectively across Canada and the United States. In addition, both countries have additional monitoring efforts being undertaken at the State and Provincial government level. However, data in this report will be confined to that from the NADP and CANSAP studies, the largest of the present efforts. The discussion will be concerned primarily with the concentration and deposition patterns for hydrogen ion and sulfate ion since these two species represent the primary variables being investigated in aquatic and terrestrial ecosystem effects research.

The CANSAP network in Canada was organized and is operated by the Atmospheric Environment Service. In the United States the NADP network is a result of an effort initiated by the State Agricultural Experiment Stations and the U.S. Department of Agriculture. It is now supported by a number of federal agencies, state agencies and private corporations. In response to the National Acid Rain Precipitation Assessment Plan to be discussed later, the NADP network in the United States will likely be increased to 125 to 150 stations. Both the NADP and CANSAP networks are planned to operate for an indefinite period of time to make possible the assessment of long-term temporal trends. The pertinent operating characteristics of these two networks are listed in Table 1.

Figure 1 presents the precipitation weighted, annual average concentration of acidity expressed as pH for the calendar year 1980. It is noted that the highest concentrations of acidity, or lowest pH levels occur in the northeastern U.S. and southern Ontario, Canada. In these regions the annual average reaches a level of approximately 4.1. As will be discussed in a later section

TABLE 1. Monitoring Design

	NADP	CANSAP
Sampling frequency	weekly	monthly (pooled events)
Collector type	wet/dry	wet/dry
Location	remote areas	remote areas
Site measurements	pH, conductivity precipitation	precipitation
Chemical analysis	pH, Ca, Mg Na K NH_3, SO_4 NO_3 Cl PO_4 (each network has single laboratory)	
Data availability	hard copy and computer tapes	

(Aquatics), a pH of 4.7 is proposed to be a minimal pH level for the protection of the more sensitive lakes and streams. It can be clearly seen (Fig. 1) that a large area of the eastern U.S. and Canada is now receiving precipitation with acidities in excess of the proposed protective limit. It is also clear that the pH of precipitation, both in the U.S. and Canada, increases as one moves in a westerly direction; the lowest acidities are encountered in the midwestern and Rocky Mountain States and Provinces. As one continues to move west, acidities again increase with peak values being encountered around the major industrial and metropolitan areas.

If one studies the sulfate ion concentration pattern as displayed in Fig. 2, simple calculations would predict that if hydrogen ion were related to the sulfate concentration, there should be a more or less steady west to east increase in acidity. (Nitrate concentrations also show a similar spatial pattern to that of sulfate.) In fact, this is not the case, even though abnormally large sulfate ion concentrations are noted in the midwest provinces of Canada and the neighboring states in the U.S. (Believed to be the result of the high sulfur content of natural gas in this area.)

The pattern of low acidity in the midwestern areas of the U.S. and Canada is readily explained by the relatively high concentrations of calcium, magnesium and ammonia present in precipitation of this region. These high levels of calcium and magnesium apparently result from suspended dust from the calcareous soils. High ammonia concentrations are presumably contributed from natural soil and plant processes. These alkaline materials are at levels sufficient to neutralize over 100% of the acidity of the sulfuric and nitric acids in the more arid regions of the western U.S. and Canada. Thus, precipitation pH values remain high.

Table 2 summarizes the data for concentrations of the major acidic and alkaline species for arbitrarily chosen regions of the United States. In the

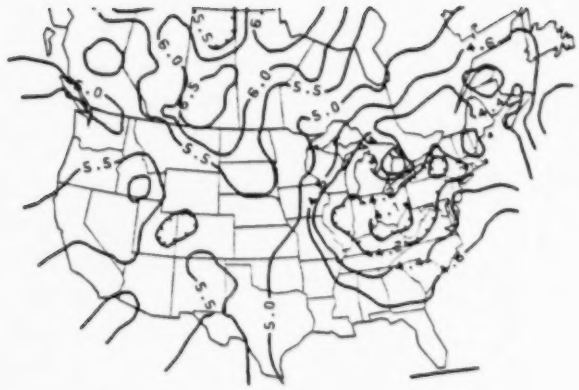

Fig. 1. Hydrogen ion concentration - pH - 1980 Annual precipitation-weighted average. (Reproduced by permission of the NADP)

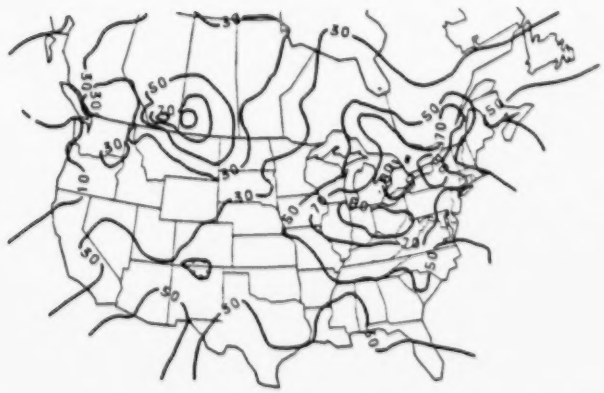
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TABLE 2. Regional Annual Averages, 1980

	pH	SO_4^*	NO_3^*	NH_4^*	CA*
"Background" Sites	5.1-5.2	5-7	2-3	1-2	2-3
Western-Midwestern	5.0-5.5	20-30	15-30	10-40	10-30
North Eastern	4.1-4.2	70-80	30-35	15-20	10-15

*Concentrations in μeq/l

west and midwest, as already noted, the sum of the calcium and ammonia concentrations, on an equivalent basis, can equal the sum of the acid anions. It is also shown in Table 2 that "remote" areas of the United States (background sites) are receiving only mildly acidic precipitation; the pH of which is still controlled primarily by the concentrations of sulfate and nitrate with minimal buffering by calcium or ammonia. Since these values represent the background levels for the western U.S. and Canada, it is evident that significant anthropogenic sources of both sulfate and nitrate occur in the western, as well as the eastern United States, and that the western United States and Canada is "protected" to some degree by extensive areas with calcareous soils. For this reason, as will be discussed later, the concern for effects of acid deposition is confined primarily to the eastern U.S. and Canada.

Figures 3 and 4 present the average annual deposition data for 1980 for hydrogen ion and sulfate ion, respectively. It should be noted in the case of hydrogen ion that acid deposition levels are low in the western areas of the U.S. and Canada due to both higher pH levels and less precipitation than in eastern North America. Much of this region receives less than 30 cm of precipitation per year as opposed to over 1 m of precipitation in many areas of the east. A pH of 4.7--the proposed protective limit--in an area with 1 m of rainfall, is equivalent to a sulfate deposition of 10 kg/ha/yr. (This does not consider nitrate levels or neutralization which is a reasonable approximation since the sum of the basic cations often is equivalent to nitrate.) The sulfate deposition values are shown in Fig. 4. It is obvious that a large area of the eastern U.S. and Canada receives sulfate deposition in excess of this protective figure with some regions receiving over 40 kg/ha/yr.

While the data shown for 1980 presents the spatial patterns of deposition, little information is available to date on temporal trends except for seasonal sulfate and hydrogen ion concentrations which appear highest in the summer months. The other components of rainfall, including nitrate, show little seasonal variation. No significant long-term trends can yet be discerned from the data from these networks which have data available for only 3 years for a

Fig. 3. Hydrogen ion deposition (wet only) - mg/m^2 - 1980 Annual average.
(Reproduced by permission of the NADP)

Fig. 4. Sulfate deposition (wet only) - kg/hectare - 1980 Annual average
(Reproduced by permission of the NADP)

limited number of sites. The pH isopleths in Fig. 1 for the eastern United States compare closely with those of Likens for the period 1972-73. While there appears to be a possible tenth of a pH unit increase in acidity in many areas during the 10-year period, this difference cannot be considered significant at this time.

EFFECTS OF ACID DEPOSITION

Agriculture

While acidification of lakes and streams was the first recognized detrimental effect of acid deposition in the United States, it was the concern for the potential effect on agricultural crops which prompted the organization of the National Atmospheric Deposition Program in the U.S. While only a small portion of the research effort in the U.S. is now agriculturally oriented, agricultural impacts are still a major area of concern.

Most research related to acid rain effects on agricultural crops focuses on direct foliar injury and potential economic losses through either decreased productivity or decreased marketability. A limited amount of research is being conducted to determine the interactive response of crop plants to acid deposition and oxidants (O_3, NO_2, SO_2). Only a few studies have been directed toward assessing plant response as influenced by changes in soil chemistry.

In the latter case, Shriner and Johnston (ref.2) have shown that no difference in effects is observed when the soil is either exposed or covered during treatment of plants with simulated acid rain. While their research represented only short-term experiments, soils are regularly amended by the farmer with fertilizers and lime at levels which far exceed even the most intense atmospheric deposition patterns. Thus, no measurable effects of acid deposition on managed agricultural soils are anticipated. Some positive responses have, however, been noted in alkaline soils with N and S deficiencies. In studies of possible synergistic effects which might result from both acid rain and oxidants in combination, limited research by Johnston et al. (ref.3) has shown that the effects appear to be additive. No synergistic responses have been detected to date.

Direct effects resulting from the exposure of plant surfaces to atmospheric deposition are generally studied by the application of sprays of simulated acid rain containing sulfuric and nitric acids mixed in a 2:1 ratio, the observed SO_4/NO_3 ratio in precipitation of the northeast. A number of laboratories involved in research on crop responses have reported conflicting results on studies of the same species (soybeans) ranging from reduced productivity to enhanced growth. When comparing data from the various research laboratories, it is clear that a number of factors are important in determining the affects of acid deposition. These include:

A. Soil type.
B. Air quality
C. Climatic differences.
D. Varietal differences of the crops studied.
E. Greenhouse versus field experiments.
F. Confounding of designs due to ambient rainfall exposures during experimentation.
G. Sulfate/nitrate ratios in simulated rain.

Evans et al. (ref.4) in studies on soybeans grown in an agriculture field in which ambient rainfall was excluded, demonstrated a reduction in yield as the pH of artificial rainfall was decreased from 5.6 to 2.3. Plants exposed to simulated rainfall at pH 4.1, 3.3 and 2.7 had decreased seed yields of 10.6, 16.8 and 23.9%, respectively, below the yields of plants exposed to simulated rainfall of pH 5.6. Field grown soybeans, however, exposed to both ambient rainfall and simulated rainfalls of pH 4.1, 3.3, 2.7 and 2.3 had decreased yields of 2.6, 6.5, 11.4 and 8.5%, respectively, indicating that the exclusion of ambient rainfall is an important parameter in assessing acid deposition effects on vegetation. On the other hand, in a greenhouse experiment, Irving (ref.5) showed that soybean dry seed weight was affected not only by pH but also by the SO_4/NO_3 ratio. This work was carried out using SO_4/NO_3 ratios of 3:1, 2:1 and 1:1 at pH 5.6, 3.8, and 3.0. In all cases, the plants treated with an SO_4/NO_3 ratio of 3:1 showed higher seed dry weight. Unlike the results of Evans, the pH 3.0 treated plants showed increased dry seed weight with 3.8 pH treatment resulting in minimum seed weight.

Research carried out by Shriner and Johnston (ref.6) has shown the importance of varietal differences. Foliar growth reduction for one variety of tomatoes was noted between 4.0 and 3.3. Growth reduction for two other varieties occurred between pH 3.0 and 2.3. Two wheat cultivars exhibited growth reduction at pH levels of 4.0 to 4.3 and growth stimulation at pH 2.3. A third cultivar exhibited small growth stimulation at all pH levels of less than pH 5.6. These experiments were carried out using 2:1 SO_4/NO_3 ratios. Studies by Lee et al. (ref.7) on numerous vegetable crops demonstrated reductions in yield, leaf damage (reduced marketability), and increased biomass, depending on the crop. As in the other research results most effects were seen when pH levels were below 3.5.

In summary, it can be stated that our knowledge of the influence of acid deposition on agricultural crops is fragmentary at best. Effects can either be of a beneficial or detrimental nature. Beneficial effects may be observed as a result of both sulfur and nitrogen fertilization. Responses vary from one region of the country to another depending on climate, soils, and factors such as SO_4/NO_3 ratios even at equivalent pH levels. The observation of these

responses in the field is complicated by influences of ozone or other oxidants as well as the pH of ambient rainfall. This leads to conflicting results from different laboratories especially when comparing greenhouse versus field studies. It can be stated, however, that detrimental effects are generally not observed in field experiments above pH 3.5 and frequently only pH 3 or below.

Forest Productivity

The potential effects of acid deposition on forests is of concern from an economic, watershed protection and aesthetic point of view. As in the case of agricultural crops, there is no clear evidence to suggest that deposition, at ambient levels, is affecting forest production. Direct foliar injury of acidic rain on forest tree species has been demonstrated only at pH ≤3 with simulated exposures. In preliminary studies by Shriner et al. (ref.8), needle senescence was observed at low pH levels. However, few studies have evaluated productivity losses from these observed effects, although they are certainly cause for concern. The direct measurement of forest productivity losses is a difficult and complex issue.

Two major studies have provided circumstantial evidence pointing to the possibility of forest productivity declines. In one study researchers are investigating the die-back of red spruce at higher elevations in New England, and in the other the decreased growth of pitch-pine in the New Jersey Pine Barrens. Work by Siccama et al. (ref.9) has shown both a reduction in growth rate, density, and basal area of red spruce between the years 1966 and 1980 in the Green Mountains of Vermont. This study included trees in all size and age classes. Die-back was noted in three zones: northern hardwood, the boreal forest and the intervening transitional forest zone. Soils data in the study area, dating back to 1965, show no pH change in the O horizon during the 15 year period. There was, however, a significant increase in copper, lead, zinc and organic matter in the forest floor with significant elevational trends in both lead and organic matter. When compared to stands of healthy trees in other areas, there appeared to be no significant difference in aluminum concentration in the forest soils, a suspected causal agent for growth decline. Natural factors which could affect tree health, including pathogens and climatic changes, have been investigated and could not be considered causal. Foliar analyses show that S/N ratios are significantly higher and potassium tissue concentrations lower in trees which are in poor condition. At this time no conclusion can be reached as to the factors causing the spruce die-back, although S/N ratios, low potassium levels, the possible role of high lead and other metals, and the mycorrhizal plant interactions are actively being investigated.

Johnson et al. (ref.10) in studies in the New Jersey Pine Barrens have demonstrated, through tree ring analysis, that there has been a dramatic reduction in the growth of pitch pine in the last 25 years. Again, this reduction in growth is independent of age. As in the case of the red spruce die-back, many factors have been investigated, including soil aluminum levels. Tree ring studies indicate the pattern of growth prior to 1955 was determined by factors very different from those occurring after 1955. It is also believed that acidic precipitation became a major atmospheric influence in New Jersey between 20 and 25 years ago. During the period in which growth has been suppressed, stream pH and tree growth rates show very similar cyclical patterns in year to year changes. Soils in this area are poorly buffered and the stream pH reliably reflects the pH of rainfall which averages 4.1. Stream pH in the region has declined since 1960 and now averages between pH 4 and 4.5. Again, no irrefutable evidence exists to relate the decline in growth rate to increasing precipitation acidity. Since rainfall and stream pH and growth rate appear to be correlated, it is suggested that acidic precipitation is a factor in the observed decline.

The results of the studies on red spruce and pitch pine suggest the possibility that there have been productivity changes in some species which cannot be related to natural causes. In order to test whether or not forest growth reductions exist over extensive areas of eastern United States, which are extensively forested and receive elevated levels of air pollutants and acidic rain, a study known as FORAST (Forest Responses to Anthropogenic Stress) has been organized to assess long-term trends. Eight research sites have been established in the eastern U.S. in areas which are presently receiving the highest levels of acid deposition and high emissions from industrial and urban areas. One site has been selected in the midwest as an unpolluted control site. Cores will be removed from 6 species at each site to determine growth patterns. Soil chemistry, foliar nutrition, and wood density will be determined. It is hoped that information gained in this study will provide additional insight into the possibility of forest productivity changes related to atmospheric deposition/air quality.

Several researchers are studying the possible effect of acid precipitation on plant pathogen response. Bruck et al. (ref.11), for example, has shown in studies on the development of fusiform rust in southern pine that increasing acid levels reduced the number of galls formed. Simulated rainfall was applied to the trees at pH 5.6, 4.0, 3.2 and 2.4 which were inoculated with fusiform rust spores. Gall formation was reduced from 2.6 per tree at pH 5.6 to 0.8 per tree at pH 2.4. These researchers have also observed decreases in soil-borne pathogen populations in simulated exposures of acidic rain.

In summary, the forest response to acid deposition is unknown at this time. Sulfur and nitrogen inputs are undoubtedly beneficial. The cause of apparent productivity declines in some species cannot be unequivocally related to acidic deposition with the research conducted to date.

Soils

Changes in soil chemistry can potentially have major impacts on forest productivity as well as the chemistry and productivity of aquatic systems. There is a need, therefore, to understand the nature of possible changes, which may be related directly to the chemical inputs from deposition as well as changes in soil biotic processes which in turn affect nutrient availability, toxic metal concentrations, and other soil chemistry properties.

Early researchers proposed that the direct response of soils to acid deposition would be the lowering of soil pH, the soil pH being controlled primarily by the soil cation exchange capacity (CEC). Recent studies by Cole and Johnson (ref.12) have shown, however, that natural acid forming processes such as the release of carbon dioxide by decomposition and root respiration may contribute several times as many hydrogen ions as precipitation. This process along with other natural processes such as organic acids formation, natural mineral weathering and leaching may be more important than atmospheric inputs in the process of soil acidification. Therefore, it is likely that adverse effects, if detected, will result chiefly from alterations of processes such as soil biochemical reactions (microbial), nutrient availability (leaching losses), organic matter accumulation, mobilization of trace elements and dissolution of clay minerals. McFee et al. (ref.13) has suggested that most soils are resistant to pH change and that there is only "a small likelihood of rapid soil degradation due to acidic precipitation." He also goes on to indicate that this is probably a short-term view and that over prolonged periods, hundreds of years, there is no way to predict acid deposition impacts due to the complexity of the soil system. However, most soil scientists seem to agree that acid deposition does increase the rate of nutrient losses and to various degrees aluminum mobility. Acid effects on each process are soil dependent.

Increased leaching of cations represents an important loss of plant nutrients and results in chemical changes in the water quality of aquatic systems into which they are ultimately discharged. While there is no doubt that acidic precipitation accelerates cation leaching rates, this needs to be evaluated along with other factors such as natural internal leaching processes, the rate of acid input and the degree to which soils are capable of buffering against leaching and the rate of nutrient recharge through mineral weathering, as shown by Cronan (ref.14). Roberts et al. (ref.15), however, found no effect

of acidic precipitation on calcium, magnesium, potassium or sodium leaching rates in a Delaware forest, which agrees with the results of Cole and Johnson (ref.12) on studies in a Douglas fir ecosystem. Andersson et al. (ref.16), on the other hand, have noted a net output of calcium from a pine forest in Sweden as well as a beech forest soil in West Germany while Cronan (ref.17) reported losses of calcium and magnesium from subalpine forests in New Hampshire, and Volk (ref.18) showed the same losses from a Florida sandhill soil. These various results emphasize the need to understand the responses of different soil types.

Johnson and Cole (ref.19) and others have demonstrated that a major factor in cation leaching is the soil sulfate absorption capacity. Sulfate adsorption can prevent leaching of cations including hydrogen and aluminum. Based on the review of available data and criteria proposed by McFee (ref.20), Wicklander (ref.21), and Johnson and Cole (ref.19), it is proposed that soils likely to undergo significant changes in basic cation composition brought about by acid inputs would have these characteristics:

1. They are not renewed by flooding or other processes.
2. They are free of carbonates to a considerable depth.
3. They have low cation exchange capacity but relatively high pH, 5.5 to 6.0 or higher.
4. They do not have the high sulfate adsorption capacity.

Since the soils of low CEC in humid climates tend to be naturally acidified, few soils meet criterion 3. When applying all criteria, it appears that accelerated loss of basic cations as a result of acid deposition is likely to be a limited problem in the United States. It is believed, therefore, effects such as the reduction in forest productivity, in the short term, are not likely to occur as a result of nutrient losses but, rather, because of aluminum toxicity. Aluminum impacts are most likely to occur in soils which are already acidic, and where acid deposition and natural acidifying processes are sufficient to increase soil water acidity, resulting in additional aluminum release. Some researchers now appear to believe that in these aluminum-buffered soils, common to the eastern U.S. and Canada, Al will be released as a function of total cation input into the system, as opposed to H^+ (acidity) alone. A more comprehensive understanding of acid deposition effects on aluminum transport is obviously needed.

Studies on soil biology have demonstrated conflicting results depending on soil physiochemical characteristics and types of organisms. It is difficult to distinguish direct effects of acidification from those which result from induced changes in the soil water solution or the leaching of toxic metals. Some soil animals appear to be negatively affected by increasing soil acidity while others appear to be stimulated. As in the case of other studies, low pH

levels were necessary to realize such effects. Wilson and Alexander (ref.22) have shown that bluegreen algae is particularly sensitive to soil acidity while green algae readily colonizes in acidic soils. It has been shown by Dennison (ref.23) that simulated acidic precipitation, of pH 4 or less, substantially reduces nitrogen fixation by the dominant nitrogen fixing lichens in a deciduous forest. Gray and Williams (ref.24) have shown that fungi become increasingly important in acidic soils as compared to neutral or alkaline soils. Generally speaking, these changes have not been studied in natural soils subjected to naturally occurring acidic precipitation. It is, however, concluded that autotrophic nitrification is reduced by artificial acid inputs but probably not at pH levels of ambient rainfall in the United States. Net nitrification may not be similarly decreased because of acid tolerance of heterotrophic nitrifiers, which may maintain the nitrogen availability for plant growth.

In many cases, the addition of nitrogen and sulfur will have a net beneficial effect on plants and soil organisms. The effects of acid deposition on the soil acidity and nutrient status will likely be small, at least in the short-term. The increase of toxic metals levels in the soil solution in some soils may be the most important factor in forest productivity reduction and could result in the increased metals levels observed in surface and ground waters.

Aquatics

Undoubtedly the most convincing evidence of detrimental responses to acid deposition are those associated with pH depressions in lakes and streams. Large areas of eastern Ontario, including New England, parts of New York State and northern sections of Minnesota are underlain by granite of the "Precambrian Shield" region. This geologic formation has produced poorly buffered soils. Sensitive lakes and streams of low alkalinity or buffering capacity are also found in many areas of the region. As seen by the pH isopleth maps in Fig. 1 and 3, this region receives rainfall of the lowest pH and has the highest acid deposition rates.

Canadian investigators Beemish and Harvey (ref.25) were the first to present evidence of pH declines in North America which they attributed to acidic deposition. The lakes studied were in the La Cloche mountains which are only 65 km southwest of the smelters at Sudbury, Ontario. During the period of their study in 1969-1971, rainfall pH levels ranged from 3.6 to 5.5 and the pH of snowmelt water ranged from 2.9 to 3.8. For 11 lakes east of the La Cloche mountains for which data were available prior to 1961, hydrogen ion had increased 10 to 100-fold by 1971. For all 22 lakes studied in the region the mean annual pH declined 0.16 units per year. Dillon et al. (ref.26)

studied 3 lakes in south central Ontario where mean annual pH of precipitation in 1978 was 3.95 to 4.38. One of the lakes showed a decline in alkalinity from 33 meq/l in 1967 to a value of 20-25 meq/l in 1977. Watt et al. (ref.27) reported on 16 lakes in Nova Scotia studied in 1955 by Gorham. They found current pH values ranging from 4.2 to 6.4. When compared to Gorham's values, all lakes showed a pH decline within the 21 year period. Also, they recorded a significant increase in conductivity of the lakes. Thompson (ref.28) in studies of three rivers in Nova Scotia also noted substantial declines in the pH (-0.8) in the years from 1954 to 1974, representing slightly less than a 10-fold increase in acidity. In the United States, Davis et al. (ref.29) reviewed data from 1,368 Maine lakes during the period 1937 to 1974. The authors indicated that the mean pH had dropped from 6.8 to 6.1, a 5.2-fold acidity increase, during the approximately 40-year period. Other studies in New England by Norton et al. (ref.30) and Burns et al. (ref.31) verify the results of Davis et. al. (ref.29). In 38 lakes studied in New Hampshire by Burns, 90% showed a decrease of pH between the late 30's and 1979; the mean pH in the 1936-1939 period being 6.7 and that in the 1979 study 6.1. Studies in New York State, particularly those of Schofield (ref.32) in the Adirondak Mountains, demonstrated pH declines in freshwaters in areas of high sensitivity or low geologic buffering capacity. Similar results have been shown for studies of several lakes in Florida by Crisman (ref.33). Surveys have also shown generally increased levels of heavy metals in lakes in New England possibly brought about by both increases in the atmospheric deposition of these metals and increased leaching of these materials to the aquatic system from the terrestrial environment. Kahl et al. (ref.34) have shown depletion of metals such as zinc in the upper layers of sediments in acidified lakes. He suggests that this is due to leaching of metals from the sediment layers and/or increased mobilization of the metals in the water, thus reducing accumulation in the sediments.

It is noted that many lakes and streams in eastern Canada and the northeastern U.S. have alkalinities less than 50 meq/l. Using models developed by Henriksen (ref.35) which relate lake pH to sulfate loading and calcium concentrations, it is predicted that the maintenance of these lakes would require that sulfate loadings not exceed 10 kg/ha/yr. In areas receiving a meter of rainfall, this represents rainfall sulfate concentrations of 20 μeq/l. Expressed as hydrogen ion equivalents, this is a pH of 4.7. Since much of this area is receiving approximately 1 meter of rainfall with a pH of 4.1 to 4.2, the current sulfate loadings in these sensitive areas range between 30 and 40 kg/ha. This suggests that the protection of the most sensitive lakes in this region would therefore require a reduction of 75 to 80% in the sulfate

concentrations in precipitation in order to increase the annual average pH to around 4.7.

There appears to be substantial evidence that there has been measurable declines in pH of lakes in sensitive areas which also receive high levels of acid deposition. While there are still some concerns about comparison of present data with historical data bases, taken as a whole, the large body of evidence points to the fact that surface waters in some areas of eastern Canada and the northeastern U.S. have been acidified. While it has been suggested that the increasing acidity may be caused by land use changes, this is refuted by studies comparing lakes in similar geologic and hydrologic settings with similar land use practices but in areas receiving lower amounts of acid deposition. Such lakes are not as acidic.

It has been well documented that when the pH of lakes and streams drops below 6, detrimental effects on the aquatic biota may be noted. In the U.S., Pfeiffer and Festa (ref.36) noted that at least 180 former brook trout ponds in the Adirondak mountains no longer supported fish populations because of acidification. A survey of 214 high elevation Adirondak lakes by Schofield (ref.37) in 1975 demonstrated that 52% had pH levels below 5 and 90% of these acidified lakes were devoid of fish populations. Comparable data from 40 of these lakes prior to 1929 indicated that in only 4% were pH levels below 5 and thus devoid of fish. In the La Cloche mountain studies, Beamish and Harvey (ref.25) demonstrated that at one of the lakes in the 1950's eight species of fish were present. By 1971, the pH had decreased from 6.8 to 4.4 and no fish existed in the lake. In Nova Scotia, 37 rivers flowing into the Atlantic Ocean had historical records which verify that they were Atlantic salmon rivers. Studies show 12 of these rivers with pH levels greater than 5.0 and 10 rivers with pH levels less than 5. Of the 12 rivers with a pH greater than 5, 1 shows statistically significant declines in fishing success since 1936, 1 a slight increase and 10 no trend. Of the 10 rivers with pH levels less than 5, 9 show a significant decline and 1 no significant trend. Major research efforts in both the United States and Canada are underway to further assess the effect on fisheries populations of acid deposition and related increases in concentration of aluminum. Less information appears to exist on the response to acidification of other biotic aquatic species. In a recent review by Singer (ref.38), he suggests that acidification brings about a reduction in primary productivity, a simplification of food chains, reduced species diversity, accumulation of detritus in the sediments, and increases in fungi populations.

SUMMARY

In summary, it is evident that much of the eastern and northeastern U.S. and eastern Canada is receiving acid precipitation at pH levels less than 4.7. Demonstrated effects to date appear to be primarily those in aquatic systems. Research on potential effects to plants and soils have demonstrated inconclusive results with respect to the current levels of acid deposition. Some plants show direct effects in laboratory and greenhouse studies when pH of simulated rainfall is held to 3.5 or less. Results in soils indicate that major changes would likely not occur at current rates of acid deposition for a period of 100 years or more. While there is evidence of decline in forest growth in some areas in the last 25 to 30 years, these declines have not been unequivocally related to acid deposition. Other areas of major research interests include those related to effects on aquatic biota and the effect of aluminum and other metals leached into the aquatic systems. All of these efforts are aimed at determining both short and long term effects which may be expected if acid deposition continues at its current rate or is increased in the future.

Such concerns have led to the development in the U.S. of an Interagency Federal plan to systematically study the effects of acid deposition and to monitor temporal and spatial trends in deposition patterns over the entire United States. This plan, known as the National Acid Precipitation Assessment Plan, was put into effect in 1981 with proposed funding for 1983 of $22,000,000 per year. The primary objective of this 10-year plan is to develop a sufficient understanding of the distribution and effects of acid deposition in order to provide sufficient data for effectively regulating emissions of both sulfur and nitrogen oxides. This effort to some degree is in response to the concern of Canada about the transboundary transport of sulfur and nitrogen oxides from the industrialized areas of the mid-west and eastern United States. These sources account for approximately half of the sulfur and nitrogen deposition in eastern Canada. The U.S. and Canada, under a Memorandum of Intent on Transboundary Air Pollution, have initiated an extensive review of currently available information to assess the extent of the problem and the extent of transport of materials to Canada from the U.S. This effort, which involves a large number of scientists in the U.S. and Canada, will result in a summary of our knowledge of atmospheric chemistry, transport and effects designed to guide both governments in future plans to ameliorate such problems. This study should be completed sometime in 1982.

REFERENCES

1. G.E. Likens, Chem. Eng. News, November 26, 1976, pp. 29-43.
2. D.S. Shriner and J.W. Johnston, Environ. Exp. Bot., 21(1981)199-209.
3. J.W. Johnston, D.S. Shriner and R. Klarer, Phytopathol. News, 12(1978)153.
4. L.S. Evans, K.F. Lewin, E.A. Cunningham and M.J. Patti, New Phytol. 89(1981)459-470.
5. P.M. Irving and J.E. Miller, J. Environ. Qual., 4(10)(1981)473-478.
6. D.S. Shriner and J.W. Johnston, personal communication.
7. J.J. Lee, G.E. Neely and S.C. Perrigan, Sulfuric acid rain effects on crop yield and foliar injury, EPA Report 600/3-80-016, 1980.
8. D.S. Shriner, M.G. Decot and E.B. Cowling, Proc. Am. Phytopathol. Soc., 1(1974)112.
9. T.G. Siccama, M. Bliss and H.W. Vogelmann, Bull. Torrey Bot. Club, (in press 1982).
10. A.H. Johnson, T.G. Siccama, D. Wang, R.S. Turner and P.H. Berringer, J. Environ. Qual., 10(4)(1981)427-430.
11. R.I. Bruck and S.R. Shafer, Phytopathology, 71(1981)864.
12. D.W. Cole and D.W. Johnson, Water Resour. Res., 13(1977)313-317.
13. W.W. McFee, J.M. Kelly and R.H. Beck, in L.S. Dochinger and T.S. Seliga (Eds.), Proc. 1st Int. Symp. Acid Precipitation in Forest Ecosystems, USDA/Forest Service Gen. Tech. Rep. NE-23, Columbus, Ohio, 1976.
14. C.S. Cronan, W.A. Reiners, R.C. Reynolds and G.E. Lang, Science, 200(1978)309-311.
15. T.M. Roberts, T.A. Clarke, P. Ineson and T.R. Gray, in T.C. Hutchinson and M. Havas, (Eds.), Effects of acid precipitation on terrestrial ecosystems, Plenum Press, New York, 1980, pp. 381-394.
16. F. Andersson, T. Fagerstrom and I. Nilsson, in T.C. Hutchinson and M. Havas, (Eds.), Effects of acid precipitation on terrestrial ecosystems, Plenum Press, New York, 1980, pp. 319-334.
17. C.S. Cronan, Oikos, 10(1980)1133-1137.
18. B.G. Volk, personal communication.
19. D.W. Johnson and D.W. Cole, Environ. Int. 3(1980)79-90.
20. W.W. McFee, Sensitivity of soil regions to acid precipitation, EPA Rep. No. 600/3-80-013, 1980.
21. L. Wicklander, in T.C. Hutchinson and M. Havas, (Eds.), Effects of acid precipitation on terrestrial ecosystems, Plenum Press, New York, 1980, pp. 239-264.
22. J.T. Wilson and M. Alexander, J. Am. Soil Sci. Soc., 43(1979)936-939.
23. R. Dennison, B. Caldwell, D. Bormann, L. Eldred, C. Swanberg and S. Anderson, Water Air Soil Pollut., 7(1977)409-416.
24. T.G.R. Gray and S.T. Williams, Soil Microorganisms, Longman, New York.

25. R.J. Beamish and H.H. Harvey, J. Fish. Res. Board Can., 29(1972)1131-1143.
26. P.B.S. Jeffries, W. Snyder, R. Reid, N.D. Yan, D. Evans, J. Moss and W.A. Scheider, J. Fish. Res. Board Can., 35(1978) 809-815.
27. W.D. Watt, D. Scott and S. Ray, Limnol. Oceanogr. 24(1979)1154-1161.
28. M.E. Thompson and M.B. Hutton, unpublished report, 1978.
29. R.B. Davis, M.O. Smith, J.H. Bailey and S.A. Norton, Verh. Int. Vrein Liminol., 10(1978)532-537.
30. S.A. Norton, R.B. Davis and D.F. Brakke, Compt. Rept. Project A-048-ME, U.S. Department of Interior OWRT, 1981, p. 90.
31. D. Burns, J.N. Galloway and G.R. Hendry, Water Air Soil Pollut., 16(1981)277-285.
32. C.L. Schofield, in L.S. Dochinger and T.S. Seliga (Eds.), Proc. 1st Int. Symp. Acid Precipitation in Forest Ecosystems, USDA/Forest Service Gen. Tech. Rep. NE-23, Columbus, Ohio, 1976.
33. T.L. Crisman and P.L. Brezonik, Paper presentation 73rd Annual Meeting, Air Pollution Control Association, Montreal, Quebec, 1980.
34. J.S. Kahl, S.A. Norton and J.S. Williams, Paper presentation American Chemical Society Meeting, Las Vegas, Nevada, 1982.
35. A. Henriksen, in B. Drablos and A. Tollan, (Eds.), Proc. Int. Conf. Ecological Impacts of Acid Precipitation, SNSF, Sandefjord, Norway, 1980.
36. M.H. Pfeiffer and P.J. Festa, Acidity status of lakes in the Adirondak region of New York in relation to fish resources, Progr. Rep., Department of Environmental Conservation, Albany, New York, 1980.
37. C.L. Schofield, Ambio 5(1976)228-230.
38. R. Singer, unpublished report.